Indian J. Phys. **76A** (6), 591-593 (2002)

IJP A
an international journal

On the paramagnetic behavior of CaS: Pr phosphors

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Received 9 May 2002, accepted 15 July 2002

Abstract Magnetic susceptibility of CaS Pr has been studied at room temperature (300°K) by varying the concentration of Pr from 0.004 to 0.120% by weight. Paramagnetic behavior of Pr ions is explained using tri/tetra valent state of Pr along with cluster hypothesis. This study shows that activator enters CaS lattice in trivalent state at lower concentration and in tetravalent state at higher concentration. Clustering of ions occurs at 0.02% by weight of Pr and above.

Keywords Magnetic susceptibility, CaS:Pr

PACS Nos. 78.55.Hx, 75.30.Cr

Alkaline earth sulphides have recently been subject of renewed interest, both theoretically [1] and experimentally [2] because of their potential as host materials for device applications such as multicolour thin film electroluminescents [3] and magneto-optical devices[4]. Lehmann and coworkers [5, 6] reported the results of a detailed and systematic investigation in CaS concluding that it is an excellent host material for efficient cathode ray tube phosphors, when activated with rare earths. A number of reports have appeared, describing properties and applications of CaS, SrS and MgS in alloy semiconductors, radiation dosimetry [7], thermally stimulated conductivity [8] and fading of thermoluminescence [9].

However, less attempts have been made to date to study magnetic behavior of alkaline earth sulphide phosphors activated with rare earth [10-12]. The magnetic behavior of phosphors depends on composition, structure and ionic state. Ozawa [13] reported the rare earth ions form solid solution with host lattice as dia/tri valent ion or as tri/tetra valent ion. The present paper reports the paramagnetic behaviors of Pr ions in CaS: Pr phosphors by measuring its magnetic susceptibility.

Phosphors were prepared by firing the mixture of sodium sulphate and sodjum thiosulphate as fluxes in high grade calcium sulphate (May & Braker, 99.99% pure) as host lattice along with carbon powder (Riedal, Germany) as the reducing agent in appropriate proportion. Praseodymium oxide (Pr_2O_3 99.99% pure Fluka, AG Switzerland) was dissolved in concentrated nitric acid (Riedal, Germany). It is further diluted in triple distilled water. Paste of all above ingredients was made and dried at 80°C and the dried mass was powdered. The charge was then fired in graphite crucible at 1000°C for two hours in a muffle furnace. Excess amount of carbon was kept in a separate crucible to ensure reducing atmosphere. After firing, it was suddenly quenched to room temperature. The phosphor so obtained was finely powdered and kept in sealed test tubes. Amount of praseodymium was varied from 0.4×10^{-3} gm to 12×10^{-3} gm per 10 gm of calcium sulphate.

Volume susceptibility of phosphors was measured using Gouy method. In this method the specimen is suspended in between the wedge shape pole pieces of an electromagnet. Change in weight of the sample with the magnetic field is noted down and volume susceptibility is calculated.

$$Mg = \tfrac{1}{2}(K_1 - K_2) A H^2, \qquad 1$$

where Mg is the change in weight with the magnetic field, K_1 and K_2 are the volume susceptibility of the sample in the glass

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tube and empty glass tube, H is the magnetic field strength and A is the inner cross section of the glass tube.

The magnetic field was produced by an electromagnet supplied by m/s Universal Scientific Co., Bombay. The pole pieces of the magnet were flat, tappered with circular cross section of diameter 2 cm and were separated by 1 cm. The current was fed to the electromagnet by a regulated D C power supply. Magnetic field was varied up to 11 kilo oersted. A special physical balance was used to measure the change in weights. The balance could measure the mass up to 10^{-4} gm. The optical scale attached to the balance is divided in to 100 divisions and a vernier scale is attached to it. The balance was so adjusted that one end of the specimen was just in the center of two pole pieces.

The glass tube of uniform bore was cut into pieces of 17cm and their inner diameter at the ends was measured in two mutually perpendicular directions with the help of traveling microscope. The tube sealed at one end with epoxy resin was weighed, filled with the phosphor and weighed again. The other end was also sealed. Its weight recorded and after switching on the magnetic field it was again weighed Change in weight was measured at different magnetic fields.

The magnetic susceptibility for the phosphors is calculated at magnetic fields of 8.5, 9.3, 9.6 and 10.3 kilo oersted and is shown in the column Nos A, B, C and D in the Table 1 respectively. Calcium sulphide phosphor with flux was found to be weakly paramagnetic in the absence of activator. This may be due to electrons trapped at S^{2-} vacancy sites. These electrons show paramagnetic behavior, otherwise all other ingredients like Ca^{2+}, S^{2-} and Na^{+} are of diamagnetic nature. Their diamagnetic behavior is surmounted by the paramagnetic behavior of these trapped electrons at the sulfur vacancy sites. Evidence of intrinsic point defects in sulphide was first obtained by Auzins *et al*[14] using EPR techniques. The sulphide vacancy, traps an electron released from lattice by photo excitation, thereby becoming a paramagnetic center[15] The susceptibility of this sample is found to decrease with magnetising field. The electrons trapped at the S^{2-} vacancy are alienated even at the lower fields. Saturation at lower fields is achieved, as electrons are lighter particles. Increase in weight of phosphor filled glass tubes was seen in all the samples. Change in weight was found to increase with activator concentration up to 0.002 gm of activator per 10 gm and then found to decrease with further increases in concentration. The typical plots of volume susceptibility at room temperature (300^0K) with activator concentration is shown in Figure 1 and magnetic susceptibility with magnetic field is shown in Figure 2. Magnetic susceptibility is fairly constant with the variation of magnetic field i.e. magnetisation of the sample varies linearly with the magnetic field in the range of measurement of magnetic susceptibility

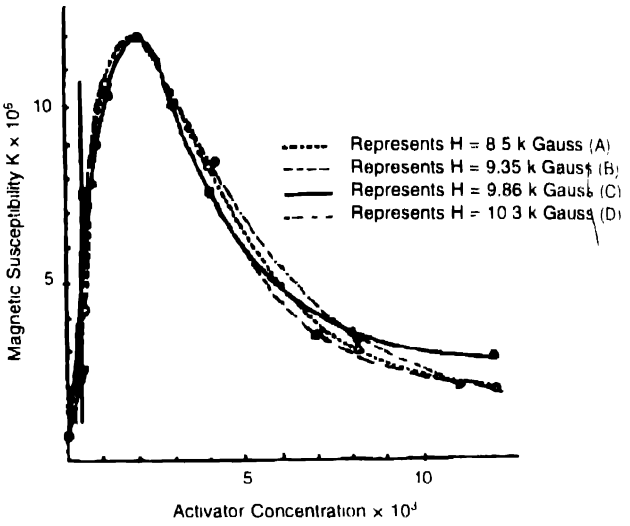

Figure 1. Magnetic susceptibility *vs* activator concentration curves at different magnetic fields

Valency of rare earth ions in host lattice is dependent on concentration, the temperature of firing[16] atmosphere in the furnace Valency change is also there due to energy of exciting

Table 1. Magnetic susceptibility at room temperature (300^0 K)

Sl No	Sample No	Concentration of activator (In weight %)	K × 10^6 CGS Units A H (8.5 K Oe)	B H (9.3 K Oe)	C H (9.6 K Oe)	D H (10.3 K Oe)
1	SD_1	NIL	0 6930	0 6843	0.6653	0.6401
2	SD_2	4×10^{-4}	2 1774	1 5353	2 3601	2.2104
3	SD_3	6×10^{-3}	7 1219	7 4619	7 2902	7 1657
4	SD_4	8×10^{-3}	8 8386	8 8655	8.8984	8.8823
5	SD_5	12×10^{-3}	10 5881	10 5058	10.2915	9 9275
6	SD_6	20×10^{-3}	11 7863	11 9811	12 1286	12.2066
7	SD_7	30×10^{-3}	10 1052	10 1593	10 2036	10 1873
8	SD_8	40×10^{-3}	8 3173	8 3981	8 4080	8.3592
9	SD_9	80×10^{-3}	3 1069	3 2609	3.4138	3 3320
10	SD_{10}	120×10^{-3}	1.9512	1.9941	1 9958	1.9258

source. Keller[17] has studied the variation of valence state of Eu using EPR and emission spectra. Preparing the phosphor in reducing atmosphere produced Eu^{2+} while preparation in an oxiding atmosphere produced decreasing amount of Eu^{2+} and increasing amount of Eu^{3+}. In our case, Pr may have entered the lattice of CaS substitutionally in both Pr^{3+} valence state and $^{4+}$ valence state as the atmosphere in the furnace may not be ully reducing. Pr^{3+} has magnetic moment 3.58 μ_B and Pr^{4+}, 2.54 μ_B [1]. At lower concentration Pr enters as Pr^{3+} predominately and this causes the increase in magnetic susceptibility with

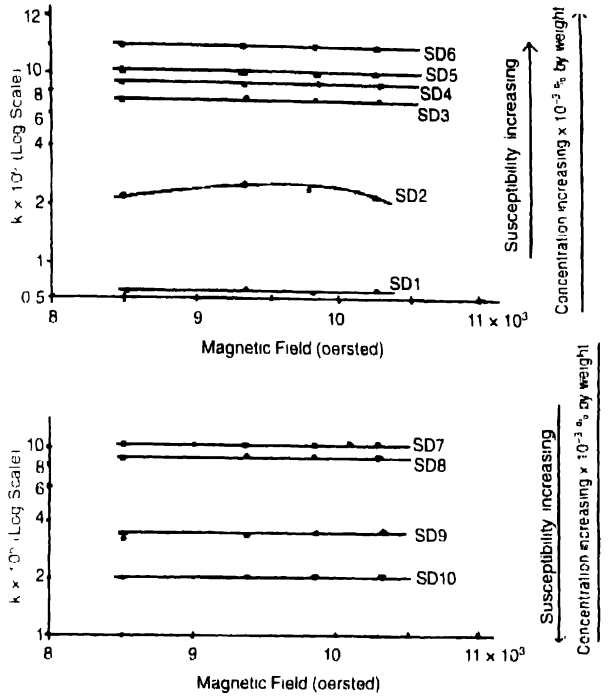

Figure 2. Magnetic susceptibility vs magnetic field curves

concentration of Pr ions, while at higher concentration, it enters as Pr^{4+} predominately causing the decrease in magnetic susceptibility with concentration. As seen in Figure 1, magnetic susceptibility increases linearly up the 20×10^{-3} % concentration of activator I Pr enters the lattice in trivalent state. The curve deviates inward in comparison to the straight line drawn, indicating that Pr ions of tetravalent state have entered the lattice. Using the relation

$$\chi = n P^2_{eff} \mu_B^2 / 3K_B T,$$

(where χ is magnetic susceptibility, n is the number of Pr ions per unit volume, P_{eff} is the effective magnetic moment, μ_B is the bohr magneton, K_B is the Boltzmann constant and T is the room temperature), slope of the straight line P_{eff} comes to be 3.5 μ_B.

Decrease in magnetic susceptibility cannot be explained fully by the above explanation alone. Another possibility may be the hypothesis of cluster formation. Smith [18] had used cluster hypothesis to explain magnetic properties of rare earth doped calcium fluoride crystals. Wapenaar [19] found ion clustering to occur at 0.01gm % of host crystal using samarium clustering of rare earth ions, reduces the total energy of the system. Energy associated with unit volume of phosphor in the magnetic field is $\frac{1}{2} \mu_i H^2$ (μ_i is the relative permeability of the phosphor and H is the magnetizing field). With the decrease of clustering energy, μ_i decreases, as a result χ also decreases. In our study, a sudden decreases in susceptibility at about 2.4×10^{-3} activator concentration, indicates clustering of Pr ions in addition to its entry in the lattice as Pr^{4+} ions. This effect is also seen in Figure 2 in which the straight line graphs of K vs magnetic field, rise up and then falls down with increase in concentration after 20.0×10^{-3} % activator concentration.

Acknowledgment

The authors are grateful to the Principal of Maulana Azad College of Technology, Bhopal, Dr S A Shaffi, Principal, Regional Institute of Education Bhopal and Dr (Mrs) S G Wanjari, Director, Kamla Nehru College, Nagpur for this constant encouragement They also thanks Dr O P Sinha for his help in carrying out the experimental work.

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